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Steam-Assisted Transformation of Natural Kaolin to Hierarchical ZSM-11 using Tetrabutylphosphonium Hydroxide as Structure Directing Agent: Synthesis, Structural characterization and Catalytic Performance in Methanol-to-Aromatics Reaction

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Supplementary Methods

ZSM-5/11 intergrowth zeolite was obtained using the same procedure of synthesizing ZSM-11-K with the aid of the tetrabutylammonium hydroxide (TBAOH, 40 wt%, Aladdin) as SDA instead of TBPOH.

Supplementary Figures and Tables

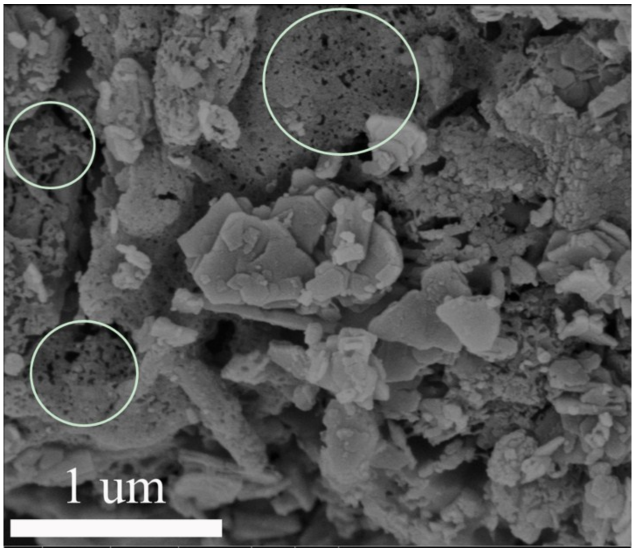

Fig. S1 SEM images of LMK

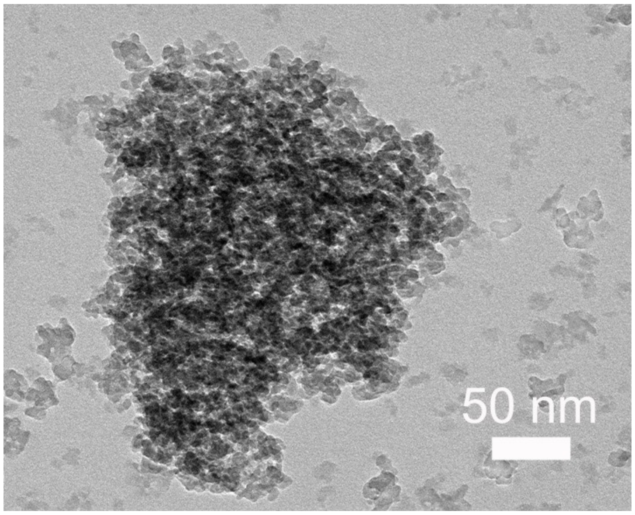

Fig. S2 TEM images of ZSM-11-K

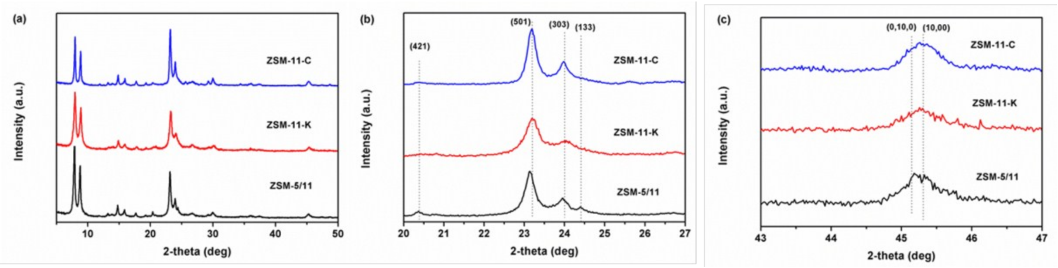

Fig. S3 (a) XRD pattern, (b) enlarged 2 θ region from 20°-27°, and (c) enlarged 2 θ region from 43°-47°.

Table S1 Chemical composition of kaolin and LMK[a]

Composition (wt%)	SiO_2	Al_2O_3	Na_2O	K_2O	Fe_2O_3
kaolin	55.3	42.5	0.09	0.42	0.70
LMK	95.3	3.4	0.06	0.24	0.09

[a] The data were determined by XRF with a Shimadzu Model XRF-1800 instrument.

Besides the characteristic diffraction peaks of ZSM-11, ZSM-5/11 exhibited the (421), (133) and (0,10,0) peaks belong to ZSM-5 (Fig. S3). It suggested that ZSM-5/11 was intergrowths of ZSM-11 and ZSM-5.[1, 2] This should be attributed to the Na^+ in LMK (Table S1). As the compresence of Na^+ could direct the formation of competing ZSM-5 phase, resultantly, a ZSM-11/ZSM-5 intergrowth is often obtained.

Table S2 Physical properties of kaolin and LMK.

Sample	Si/Al[a]	S_{BET}[b] (m^2/g)	S_{meso}[c] (m^2/g)	V_{total}[d] (cm^3/g)	V_{micro}[c] (cm^3/g)	V_{meso}[e] (cm^3/g)
kaolin	1.1	29	-	0.16	-	-
LMK	23.5	365	325	0.47	0.03	0.44

[a] Determined by XRF with a Shimadzu Model XRF-1800 instrument. [b] BET method. [c] *t*-plot method. [d] Volume adsorbed at $p/p_0 = 0.99$. [e] $V_{meso} = V_{total} - V_{micro}$.

Kaolin showed the low S_{BET} of 29 m^2/g and a Si/Al ratio close to 1, which was consistent with several research groups.[3-5] The Si/Al ratio was increased from 1.1 to 23.5 for kaolin by acid leaching. Moreover, the LMK exhibited high S_{BET} of 365 m^2/g and rich V_{meso} of 0.44 cm^3/g. Notably, it has been proposed that acid leaching mainly resulted in dealumination of kaolin and hence created mesopores on kaolin.[6, 7]

Table S3 Acid properties of ZSM-11-C and ZSM-11-K.

Sample	Acidity by strength[a] (μmol/m^2)			Acidity by type[b] (μmol/m^2)		
	SAS	WAS	Total	LAS	BAS	Total
ZSM-11-C	2.144	1.619	3.763	0.800	1.146	1.946
ZSM-11-K	1.320	1.379	2.708	0.502	1.120	1.622

[a] The concentration of strong acid sites (C_{SAS}) and weak acid sites (C_{WAS}) determined by NH_3-TPD.

[b] The concentration of Lewis acid sites (C_{LAS}) and Brønsted acid sites (C_{BAS}) calculated by Py-IR after evacuation at 350 ˚C.

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